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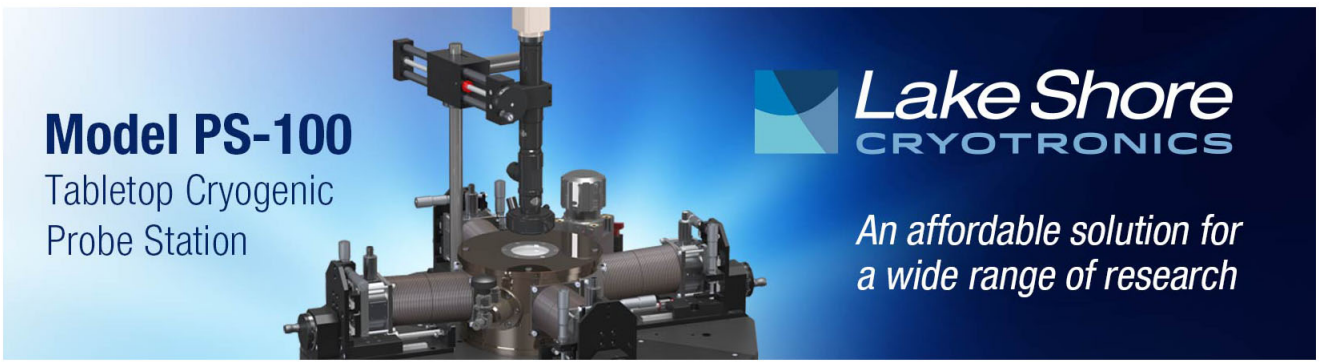

A photoelectron spectroscopy study of the electronic structure evolution in $CuInSe_2$-related compounds at changing copper content

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Evolution of the valence-band structure at gradually increasing copper content has been analysed by x-ray photoelectron spectroscopy (XPS) in In_2Se_3, $CuIn_5Se_8$, $CuIn_3Se_5$, and $CuInSe_2$ single crystals. A comparison of these spectra with calculated total and angular-momentum resolved density-of-states (DOS) revealed the main trends of this evolution. The formation of the theoretically predicted gap between the bonding and non-bonding states has been observed in both experimental XPS spectra and theoretical DOS. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4752723]

$CuInSe_2$ is a chalcopyrite semiconductor compound used in the absorber layer of thin-film solar cells. Currently, $CuInSe_2$-based photovoltaic devices with the structure ZnO/ CdS/ $Cu(InGa)Se_2$/Mo hold the leading position in terms of performance and stability amongst thin-film technologies. For laboratory scale, the record conversion efficiencies of $CuInSe_2$-based solar cells exceed 20%.[1] Despite such a success a number of fundamental issues concerning the materials physics remain unresolved.

The presence of copper appears to be critical for a number of phenomena which make $CuInSe_2$ and related chalcopyrites good electronic materials for the absorber-layer application. The uppermost valence band (VB) in $CuInSe_2$ is formed by hybridised Se 4*p* and Cu 3*d* states.[2] The repulsion between the Se *p* and Cu *d* states pushes the valence band maximum up and the conduction band minimum down, thereby significantly reducing the band gap in $CuInSe_2$ in comparison with its binary analogue ZnSe. The electrical passivation of the antisite defect In_{Cu}, main compensating donor at Cu deficiency, by the formation of the neutral defect complexes $2V_{Cu} + In_{Cu}$ with negative formation energies, provides an opportunity to dope $CuInSe_2$ by the shallow acceptor, copper vacancy V_{Cu}, by shifting the elemental composition towards In excess.[3] The copper depleted compounds $CuIn_3Se_5$ and $CuIn_5Se_8$, also called ordered defect compounds (ODCs),[4] are formed at copper deficiency. Their structure can be produced by repeating $2V_{Cu} + In_{Cu}$.[3] Copper deficient *n*-type conductivity layers have been observed on the surface of $CuInSe_2$ prior to the deposition of CdS buffer layer suggesting that ODC compounds play a vital role in the formation of *p*-*n* junction.[4] To improve the performance of the $CuInSe_2$-based solar cells further, we should understand how the electronic structure of $CuInSe_2$ is changing at copper deficiency.

Despite the importance of this topic, the electronic structure of ODC has been studied mostly theoretically.[2,3,5] X-ray photoelectron spectroscopy (XPS) is one of the most direct methods for analysing the electronic structure of solids. However, very few reports can be found in the literature on XPS studies of the ODC compounds. An experimental XPS study of In_2Se_3, $CuIn_3Se_5$, and $CuInSe_2$ thin films indicated significant differences in their valence band spectra although revealing mostly non-resolved features.[6] XPS spectra of vacuum cleaved surfaces of high structural quality single crystals can reveal an improved picture of the real electronic structure. A comparison of such XPS spectra with theoretically calculated densities of states (DOS) would provide a better understanding of the valence band evolution under the influence of the copper content.

In this report, we reveal the main trends of the evolution of the electronic structure in ODC at gradually increasing copper content by analysing experimental XPS spectra of In_2Se_3, the ODC $CuIn_3Se_5$, $CuIn_5Se_8$, and $CuInSe_2$ and comparing them with the calculated total DOS, as well as with the angular-momentum resolved local DOS. The formation of the repulsion gap between the bonding and non-bonding states of the DOS theoretically predicted in $CuInSe_2$ has been experimentally observed.

Single crystalline ingots of In_2Se_3, $CuIn_5Se_8$, $CuIn_3Se_5$, and $CuInSe_2$ were grown by the vertical Bridgman technique from near stoichiometric mixes of 99.999% purity elements in quartz ampoules sealed under vacuum.[7] Single crystalline bulk samples were taken from the middle parts of the ingots.

The structure and the unit cell parameters have been characterised by the x-ray diffraction (XRD) technique as

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described in details in Ref. 8. All the samples were found to be single phase crystals. In_2Se_3 and $CuIn_5Se_8$ were determined to have hexagonal structures, whereas $CuIn_3Se_5$ and $CuInSe_2$ had a thiogallate and chalcopyrite structures, respectively. In general, it should be noted that variations of the copper content in $CuIn_{2m+1}Se_{3m+1}$ compounds corresponding to different m results in the formation of different types of structure.

The XPS measurements were carried out using monochromated Al K_α line: $h\nu = 1486.6$ eV at the Department of Physics, University of Osnabrück. The analysed samples were cleaved under high vacuum conditions in preparation chamber and then moved for XPS measurements without breaking vacuum. All the XPS spectra were measured under ultrahigh vacuum $\sim 2 \times 10^{-10}$ Torr using PHI 5600ci spectrometer with the total-energy resolution set to 0.2 eV. No noticeable charges of the sample surfaces by high-intensity Al K_α beam has been observed during the measurements. In order to improve the quality, all the analysed XPS spectra have been deconvoluted using a Gaussian line shape with the standard full width at half maximum (FWHM) of 0.34 eV.[9]

The presence of oxygen on the surface during the experiments was monitored by measuring the intensity of the 1*s* oxygen line in the spectra before and after the experiment. The registered increase in the concentration of oxygen was very small and did not affect the shape of the spectral lines. The energy calibration during each cycle of the measurements has been performed using the 4*f* states of an Au foil kept in contact with the analysed sample. All the measurements were carried out at room temperature.

The atomistic modelling of the chalcopyrite-type $CuIn_{2m+1}Se_{3m+1}$ compounds and hexagonal In_2Se_3 was based on the first-principles projector-augmented wave method[10] within the density functional theory (DFT), as implemented in the VASP package.[11] Calculations of the DOS were performed with the hybrid functional approach by Heyd *et al.* which yields very reasonable band gap energies and DOS.[12] The plane wave energy cutoff was 350 eV. The irreducible Brillouin zones are sampled by Γ-centered Monkhorst-Pack type **k**-mesh (20–30 **k**-points) and integrated by tetrahedron method with Blöchl corrections. Whereas the crystal unit cells of $CuInSe_2$ and $CuIn_5Se_8$ are well established, there are different proposed structures for $CuIn_3Se_5$. In this work, we are interested in studying the impact on the valence band energies due to changes in the [Cu]/[In] ratio, and we therefore model the $CuIn_3Se_5$ with the compositionally comparable $Cu_5In_9Se_{16}$ phase.

The experimental XPS spectra of the top of the VB in In_2Se_3, $CuIn_5Se_8$, $CuIn_3Se_5$, and $CuInSe_2$ are shown in Fig. 1 on a binding energy scale. Calculated total DOS, for these compounds, presented with a 0.3 eV Lorentzian broadening, are also shown in Fig. 1 on the energy scale referring to the valence band maximum.

To understand the role of copper, we analyse the electronic structure in the two ODC $CuIn_5Se_8$ and $CuIn_3Se_5$ comparing the observed changes with that in $CuInSe_2$ in terms of the four band structure theoretically predicted by Jaffe *et al.*[2] and demonstrated by Zhang *et al.* in a calculated total DOS for $CuInSe_2$.[3] This structure is shown in Fig. 1(d) for the XPS spectrum in $CuInSe_2$.

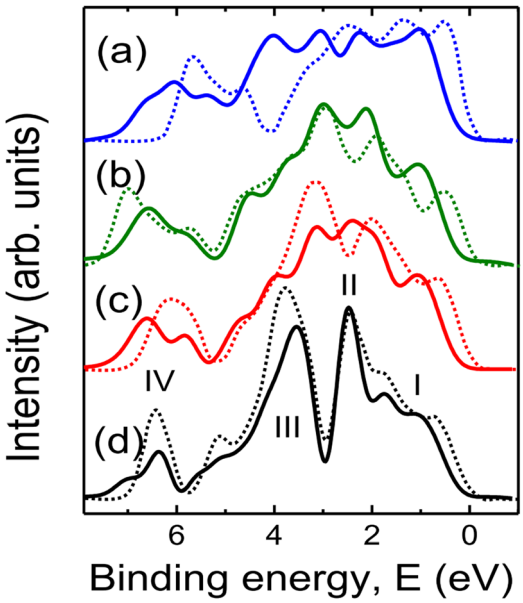

FIG. 1. Solid lines are experimental XPS spectra of the VB in In_2Se_3 (a), $CuIn_5Se_8$ (b), $CuIn_3Se_5$ (c), and $CuInSe_2$ (d): dependence of the photoelectron intensity $I(E)$ on the binding energy E. Dotted lines are the calculated total DOS, presented with a 0.3 eV Lorentzian broadening and where the energy scale refers to the valence band maximum.

According to Ref. 3, band (I) at 0.8 eV is formed by the anti-bonding part of the hybridised Se *p*- and Cu *d*-states. The deeper non-bonding part (II) at 2 eV dominates the total DOS of $CuInSe_2$. The bonding part of the Se *p*- Cu *d*-states (III) at 4.3 eV is separated from the non-bonding one by a considerable gap of 0.5 eV. The last part of the structure (IV), formed mostly by the In *s*- and Se *p*-states, is also separated from the top VB by a gap.

The In_2Se_3 XPS spectrum can be seen in Fig. 1(a). It constitutes two major features: a higher intensity dominant broad topmost band and a lower intensity deeper band at 6 eV. The calculated angular-momentum resolved local DOS spectra of these compounds, shown in Fig. 2(a), suggest that the dominant broad band is formed mostly of the Se *p*-states with a small admixture of In *p*-states, whereas the deeper band consists of the In *s*-states with a smaller fraction of Se *s*- and *p*-states. The calculated total DOS in Fig. 1(a) generally resembles the experimental XPS spectrum. Differences between them can be related to the influence of the photoionisation cross section of electrons which is not taken into account in calculated DOS.

The presence of copper in $CuIn_5Se_8$ can be clearly seen in the XPS spectra shown in Fig. 1(b) as the appearance of a double peak at the centre of the topmost part of the VB. The theoretically calculated total DOS, also shown in Fig. 1(b), agrees with this spectrum excellently reproducing all the features of the experimental spectrum. The content of different states in the DOS is shown in Fig. 2(b). It is apparent that Cu is becoming its major component and mostly represented in the topmost part of the VB by its *d*-states. Although the Se *p*-states and In *p*-state fractions are significant this part of the VB in $CuIn_5Se_8$ has acquired the four band structure.

These four bands, denoted as I, II, III, and IV, are shown in Fig. 2(b). The (I) band is presented in the XPS spectrum by a resolved peak. The Cu *d*- and Se *p*- present in this band

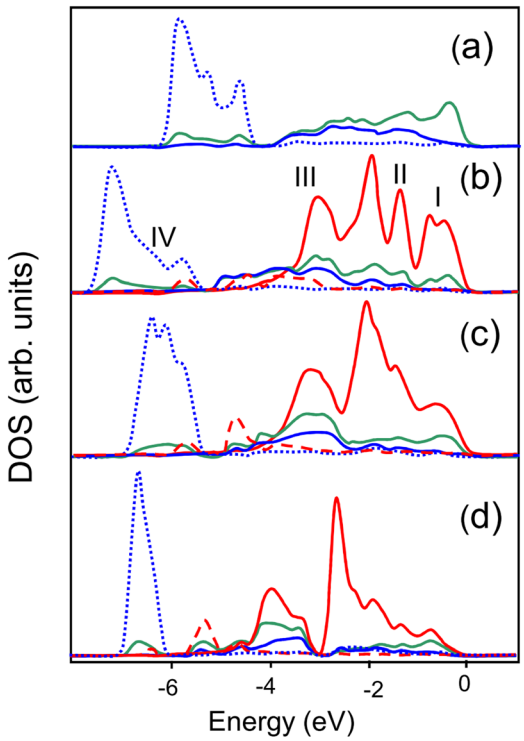

FIG. 2. Calculated angular-resolved local DOS in In_2Se_3 (a), $CuIn_5Se_8$ (b), $Cu_5In_9Se_{16}$ (c), and $CuInSe_2$ (d), where blue dotted lines are In *s* states, blue solid lines are In *p* states, green solid lines are Se *p* states, red dashed lines are Cu *s* states and red solid lines are Cu *d* states. The energies refer to the valence band maximum.

are almost split from the rest of the VB suggesting that this band is a separate feature associated by Zhang *et al.*[3] with the antibonding Cu *d*- and Se *p*-states. The two deeper bands (II) and (III), associated in Ref. 3 with the non-bonding and bonding part of the hybridised states, are also present in both the XPS spectrum and total DOS shown in Fig. 1(b) as the dominant double peak revealing well seen signs of splitting. Although, as it can be seen in Fig. 2(b), this peak is dominated by the hybridised Cu *d*- and Se *p*-states both these as well as a small fractions of the In *p*- and Cu *s*-states are becoming structured forming a gap at 3 eV. The band (VI), formed mostly of the In *s*- and Se *p*-states with a small admixture the Cu *s*-states, is also affected by the presence of the Cu *d*-states by shifting deeper in comparison with In_2Se_3. This shift can be well seen in both, the experimental XPS spectrum and theoretical total DOS shown in Fig. 1(b).

A further increase of the copper content in $CuIn_3Se_5$ does not change much the shape of the XPS spectrum in $CuIn_3Se_5$ shown in Fig. 1(c). It retains the four band structure however the (II) band associated with the non-bonding states is becoming dominant which is not clear in the theoretical total DOS, although the state content in Fig. 2(c) demonstrates an increase of the Cu *d*-state fraction, which reveals a prominent maximum at 2 eV which probably can be related to the non-bonding state (II) band. The deepest part of the (III) band is not well resolved in the experimental XPS spectrum in Fig. 1(c), although from Fig. 2(c) it is clear that this is a separate feature which is dominated by the Cu *s*-states also containing Se *p*- and a small fraction of the In *p*-states. This feature is not formed in $CuIn_5Se_8$ due to a lack of the Cu *d*-state content. The increased copper concentration in $CuIn_3Se_5$ and then in $CuInSe_2$ results in pushing the Cu *s*-states into this feature.

In $CuInSe_2$, the copper content increase results in significant changes in the XPS spectrum shown in Fig. 1(d). The very top (I) band becomes less resolved, whereas the (II) band becomes very sharp revealing a deep gap at 3 eV between the (II) and (III) bands. The (IV) band is shifting deeper from the VB top. The theoretical total DOS excellently reproduces all the features of the experimental XPS spectrum. The local DOS, in Fig. 2(d), shows that the (I) band representing the antibonding part of the DOS contains equal fractions of the Cu *d*- and Se *p*-states, whereas In *p*-states are almost absent. The (II) non-bonding band contains mostly Cu *d*-states which are split from the (III) bonding ones. The (III) band becomes clearly structured with the top part, containing equal fractions of the Cu *d*- and Se *p*-states with small admixture of the Cu *s*- and In *p*-states, and the deeper part containing the Cu *s*-states also containing Se *p*- and a small fraction of the In *p*-states. The split off (IV) band dominated by the In *s*-states and some admixture of Se *p*- and Cu *s*-states. With increasing Cu content, this band is pushed deeper from the topmost VB and becoming sharper.

Experimentally observed in the XPS spectra of $CuInSe_2$ and other chalcopyrites, the four band structure has been reported by Rife *et al.* and later in a number of publications.[13] However, the gap between the (II) non-bonding band and the (III) bonding band well seen in the theoretical DOS of $CuInSe_2$ not always can be found resolved in the XPS spectra. We relate this peculiarity to the quality of the material and the surface which has been cleaned by one of the following techniques: more damaging ion beam sputtering requiring subsequent annealing and less damaging cleavage under vacuum or by Se capping-decapping.[14]

The observed changes in the VB structure of the four compounds suggest that the degree of *p-d* hybridization is directly determined by the copper content and by decreasing the concentration of copper the repulsion of the bonding and non-bonding states can be tuned.

In conclusion, evolution of the VB structure at gradually increasing copper content has been analysed by studying XPS spectra in In_2Se_3, $CuIn_5Se_8$, $CuIn_3Se_5$, and $CuInSe_2$ single crystals. A comparison of these spectra with calculated total DOS and angular-moment resolved local DOS revealed the main trends of this evolution. The formation of the theoretically predicted gap between the bonding and non-bonding states in the DOS has been observed in our experimental XPS spectra.

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